

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No. 11371

Authorized Officer: Jeannette Washington)
PCT International Division)
Applicant: Enthone-OMI Inc)
International Application No. PCT/US00/16324)
International Filing Date: 12 July 2000)
Title: "PROCESS FOR PLATING)
PLASTICS USING A)
CATALYTIC FILLER")

RESPONSE TO
NOTIFICATION OF
STATUS OF
REQUIREMENTS
UNDER 35 U.S.C. 371

Assistant Commissioner of Patents
Box PCT
Washington, D.C. 20231

RECEIVED

06 DEC 2001

International Division

Attn.: RO/US

Sir:

This is in response to the "Notification of Status of Requirements Under 35 U.S.C. 371" mailed on 31 July 2000 in the above-identified application by the U.S. Patent and Trademark Office, as the Designated Office.

This Notification stated that before U.S. National processing could begin, the following items had to be received by "DO/EO/US" before the expiration of the applicable time limit:

- a) c.1. - U.S. National Fee;
- b) c.2. - Oath or Declaration;
- c) c.5. - Amendments under PCT Article 19, if any.

With regard to item a) above, please charge our Deposit No. 15-0900 for this amount of the U.S. National Fee. A duplicate copy of this sheet is enclosed.

With regard to item b) above, in a telephone conference with Jeannette Washington, the Authorized Officer for this application, on 22 August 2000, it was noted that the Oath/Declaration had been included as part of the application as originally filed. Upon rechecking the application file, Ms. Washington confirmed this was the case, and that nothing further was

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required in regard to this item. A duplicate copy of the Declaration as filed is enclosed for reference.

With regard to item c) above, at this time Applicant has no amendments to the claims under PCT Article 19.

If there are any questions with regard to the above, please contact the undersigned at 810-497-6892.

Respectfully submitted,
Enthone-OMI Inc.

By: Richard P. Mueller
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Dated: August 28, 2000

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to :Assistant Commissioner for Patents, Box PCT, Washington, D.C. 20231, Attn: RO/US on August 29, 2000.

By: Ann D. Griggs
Ann D. Griggs

09/673832

Title: Process for plating plastics using a catalytic filler.

The present invention relates to an improved process for plating plastics using a catalytic filler. More specifically, the present invention relates to electroless plating.

5 There is a growing need for plating non electrically conductive plastic surfaces with metals for application in e.g. circuit boards, shields for electromagnetic radiation in electronic devices, etc.

10 To obtain the desired metal plating of plastics, electroless plating using a catalytic material which is present on the surface of the article to be plated can be applied. The catalyst usually comprises PdCl_2 , silver compounds or ferrous phosphides, which are present in the form of small particles on the surface of the article to be
15 plated. In order to deposit the metal, the article is submerged in a solution of a salt of the desired metal and an appropriate reducing agent. Under suitable conditions the catalyst particles cause the metal ions to be reduced from the solution to form a metal plating. This step can be
20 followed by one or more additional electroless plating steps, using additional solutions or by conventional electrochemical plating steps. In this way a plating of the desired thickness can be obtained.

25 A common technique to apply the catalyst material to the surface of the article is by using a lacquer in which the catalyst material is present. Usually such a lacquer comprises acrylic resins, polyurethane (PUR) (crosslinked or non-crosslinked) resins, and the like. After applying the liquid lacquer to the article, it is heated, which causes the
30 solvent to evaporate and, subsequently, the resin to harden. This type of plating proves effective for plating acrylonitrile-butadiene-styrene copolymer (ABS), polycarbonate (PC) blends, PC and others.

35 Another technique to apply the catalyst material, which technique generally uses Pd salts, is to dip the

pretreated plastic parts in a palladium based activator solution. After the proper pretreatment the catalyst will absorb onto the polymer surface.

An obvious drawback of the first mentioned technique is that it is difficult or even impossible to plate articles with surfaces that are not easily accessible for the lacquer. For example, drill holes in printed circuit boards or articles having a complex geometry cannot be coated successfully with a lacquer filled with catalyst. Selective plating can only be achieved by using masking techniques when applying the lacquer. The second technique, which uses immersion in catalyst solution, does not provide any selectivity at all.

Another disadvantage is the requirement that adhesion of the lacquer has to be sufficiently strong. This cannot be achieved for all types of polymer. For example, liquid crystal polymers like Vectra® E 820 I and polymers like poly(butylene terephthalate) (PBT), polyethylene (PE), polypropylene (PP) or nylon cannot be successfully plated using a lacquer filled with catalyst.

An alternative approach for the metal plating of plastic articles is the mixing in the bulk of the plastic of the article to be plated, followed by the above mentioned electroless plating step, optionally followed by another electroless or an electrochemical plating step.

US-A-4,767,665 discloses an electroless plating process for plastic materials. The plastic articles described in this patent are prepared by compounding metallic phosphide compounds in the plastic article.

According to US-A-4,767,665 the metallic particles are exposed by carrying out a surface treatment, such as a mechanical or thermal treatment. This is then followed by plating by means of the above mentioned electroless process, e.g. by placing the articles in baths of copper salt solutions in case a copper plating is desired.

The method disclosed in US-A-4,767,665 does not solve the above-mentioned problem of plating surfaces of complex shaped articles.

Plating surfaces of complex shaped articles is of particular relevance in plating moulded interconnected devices in which often complex structures appear, which in addition require selective plating. It is also relevant for through hole copper plating of printed circuit boards.

Moreover, all of the known processes for plating plastics using catalytic fillers have in common that the initiation process of electroless plating is slow. This is reflected in the period of time that is required to observe the first signs of metal deposits. Usually this is 20 minutes or more.

In addition, with known plating techniques the means of achieving selectivity for the metal to deposit on the treated regions of the surface are limited, resulting in a final product with an insufficient resolution, unless laborious phototechniques are used. This is especially of importance in the production of printed circuit boards and moulded interconnected devices.

The present inventors have found that when the surface treatment required to expose the catalytic particles is performed using an alkaline solution, and this is followed by an activation of the exposed particles by a treatment with acid, the problems mentioned above can be overcome.

According to the present invention a plating process is provided comprising the following steps:

- a) compounding a granular plastic with a catalyst suitable for an electroless plating reaction, optionally with one or more fillers,
- b) forming a shaped body from the product of step a),
- c) removal of at least part of the material from the surface of the product of step b) to expose part of said catalyst,

- d) treatment with an acid to activate the exposed catalyst of step c), and
- e) metal plating of the product of step d) in an electroless metal bath.

5 To form moulded interconnected devices, second and further moulding steps using a non-filled plastic may be carried out between steps b) and c), providing selectivity.

Using the process according to the invention, a plating rate of about 2 $\mu\text{m/h}$ or higher can be obtained. In addition, the time in which initial deposition of metal is observed is less than about 15 minutes, and sometimes even less than about 10 minutes.

It is also possible to obtain a good and selective plating on complex shaped articles.

15 According to the present invention the removal of the plastic in step c) is preferably carried out by dissolving the plastic using an alkaline solution. Alternatively any other suitable removal technique can be used.

Suitable plastics that can be used for the plating process according to the invention are polymers which are known to be attacked by alkaline solutions. When treating such plastics with strong alkaline materials such as sodium hydroxide, the catalyst particles incorporated therein are partly set free. If such a treated material is brought in an electroless plating bath a better initiation is obtained, and the copper adheres better to the plastic. Preferred are liquid crystal polymers (LCP), such as Vectra® E 820 I, A 530, C 810, or other liquid crystal polymers sold under the registered trade names Ekkcel, Xydar and Utrax, which are all based on long chain macromolecules of acrylate copolymers comprising reinfacing groups such as p-hydroxy benzoate or 2,6-naphthalene diacids or -diols; etc., or a polymer chosen from the group consisting of ABS, ABS/PC, poly(ethylene imine) (PEI), polystyrene (PS), polyethyl-ether-ketone (PEK), polyether sulphone (PES), rubbers, nylon, poly(ethylene terephthalate) (PET) poly(butylene terephthalate), or blends

like PC/LCP or PBT/PC. Particularly preferred are PBT, PC, LCP and alkaline etchable nylons.

In step (a) the granular plastic is compounded with a catalyst. In this step fillers optionally may be present.

5 Suitable fillers are glass particles, dolomite, graphite, phosphates, sulfates, or more in detail, sulphates, phosphates and carbonates of potassium, barium and/or calcium. Fillers are added to improve mechanical strength, for coloring, as flame retardant, as "etchable" component or
10 just as a cheap bulk material to lower the price of the material to be made.

Following the exposure step, the acid treatment is performed to activate the exposed particles. Acids that are suitable for this purpose are chosen from the group
15 consisting of solutions of strong mineral and/or organic acids with a pH of below 2, preferably <1. Acids which can suitably be used in step (d) are sulphuric acid, hydrochloric acid, methane sulphonc acid, sulphamic acid, acetic acid, glycine, phosphoric acid, oxalic acid, naphthalene sulphonc
20 acid, maleic acid, benzene sulphonc acid, trichloro acetic acid and chromic acid.

The catalyst material which is present in the plastic comprises phosphides, preferably ferrous phosphides, optionally mixed with other catalytic compounds, such as
25 silver compounds, for example AgNO₃, or organo silver compounds; palladium compounds or metals such as palladium, nickel, silver or mixtures thereof.

In a preferred embodiment, the forming of a shaped body in step b) is carried out by injection moulding.

30 The invention will now be illustrated with examples, which are not intended to limit the scope of the invention.

EXAMPLE 1

Samples of Vectra® E 820 I were compounded with
5 ferrous phosphide in an amount of 15 weight-%, drawn on the
total composition, using a screw extruder. The samples were
subsequently etched using a sodium hydroxide solution of
ca. 10 N, at 70°C, 15 minutes followed by activation at room
temperature using sulphuric acid of ca. 6% for 1 minute.

10 The samples were submerged in a chemical copper bath
(Enplate™ Cu 872 I/873) at 46°C and the plating rate was
monitored.

After 5 minutes the first sign of copper deposition
was observed. After 12 minutes a closed, viz. continuous
15 metal layer was observed.

The plating rate was 2-2.5 µm/h and the final copper
thickness was 20 µm.

The plated samples were subjected to the ASTM 3359-83-
B tape test, wherein the binding between the plated metal
20 layer and the substrate layer is evaluated. From this test,
it becomes clear that the binding is good (grade 4 to 5 on a
scale of 0 to 5).

25

EXAMPLE 2

Samples of Vecta® E 820 I filled with ferrous
phosphide were prepared as in the previous example. This
material was formed into plates, in which plates holes of
30 different length and diameter were drilled. The holes were
wider than 0.15 mm. Part of the holes were etched with 10 N
sodium hydroxide. Part of the holes from the etched portion
were treated with sulphuric acid 2.5%.

The following results were obtained:

Holes	Time to first sign of copper [minutes]	Plating rate [$\mu\text{m}/\text{h}$]
non treated	∞	0
only etched	$\geq 15^*)$	$2^{**})$
etched and acid treated	5	2

*) : Depending on time between etching and plating.

5 **) : Once the initiation is complete.

Claims

1. Process for electroless plating of plastics comprising the steps of:
 - a) compounding a granular plastic with a catalyst suitable for an electroless plating reaction,
 - 5 b) forming a shaped body from the product of step a),
 - c) removal of at least part of the material from the surface of the shaped body of step b) to expose part of said catalyst,
 - 10 d) treatment with an acid to activate the exposed catalyst of step c), and
 - e) metal plating of the product of step d) in an electroless metal bath.
2. Process according to claim 1 in which the removal of the plastic of step c) is carried out by contacting the
15 shaped body with an alkaline solution.
3. Process according to claim 1 or claim 2, wherein step b) is carried out by injection moulding.
4. Process according to any of the preceding claims in which the acid in step d) is a solution of a mineral and/or
20 an organic acid with a pH of less than 2, preferably less than 1.
5. Process according to any of the preceding claims in which said catalyst comprises phosphides, preferably ferrous phosphides, optionally mixed with silver, silver compounds,
25 palladium, palladium compounds, nickel or mixtures thereof.
6. Process according to any of the preceding claims in which the plastic is a liquid crystal polymer chosen from the group consisting of a polyacrylate copolymer such as [Vectra E 820 I, A 530, C 810, acrylonitrile-butadiene-styrene
30 copolymer, acrylonitrile-butadiene-styrene

copolymer/polycarbonate blends, polycarbonate, poly(ethylene imine), polystyrene, poly(ethylether ketone) (PEK), polyether sulfphone (PES), rubbers, nylon, poly(ethylene terephthalate), and blends thereof.

- 5 7. Process according to any of the preceding claims in which the metal to be deposited from the metal bath is selected from the group consisting of copper, nickel, silver, cobalt, gold, palladium, tin, and mixtures thereof.
8. Process according to any one of the preeceding claims,
10 wherein in step (a) also a filler is compounded with the plastic and catalyst.

DUPLICATEDocket No.
11371

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"PROCESS FOR PLATING PLASTICS USING A CATALYTIC FILLER"

the specification of which

(check one)

☒ is attached hereto.

☐ was filed on _____ as United States Application No. or PCT International Application Number _____ and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority	Not Claimed
99 202 376.2	Europe	16/7/99		<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)		
_____	_____	_____		<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)		
_____	_____	_____		<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)		

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

_____ (Application Serial No.)	_____ (Filing Date)
_____ (Application Serial No.)	_____ (Filing Date)
_____ (Application Serial No.)	_____ (Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)

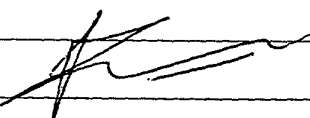
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

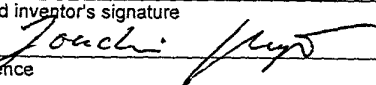
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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